

Attorney Docket No. 2003B005/2

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No. : 10/717,865
Inventor : Palanisamy ARJUNAN
Filing Date : November 19, 2003
Title : Diene-Modified Propylene Copolymers
Group Art Unit : 1713
Examiner : Roberto Rábago
Confirmation No. : [NUMBER]

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OCT 05 2006

DECLARATION UNDER 37 CFR § 1.131

I, Palanisamy Arjunan, hereby declare that:

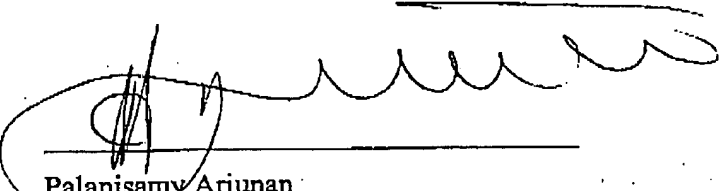
1. I am the named inventor of the subject matter described and claimed in the above-identified U.S. Application No. 10/717,865 filed November 19, 2003.
2. I conceived and reduced to practice in the United States of America the invention as shown and described in the above-identified application prior to the date May 3, 2002, the filing date of U.S. Patent Application No. 10/476,646 to Lehmus *et al.*
3. Prior to May 3, 2002, I prepared a document attached as **EXHIBIT A** that represents the reduction to tangible form of my mental concept of the invention as shown and claimed in the above-identified application.
4. **EXHIBIT A** is a document entitled "Patent Memorandum" that describes compositions of the claimed invention and properties and methods of making the claimed invention as evidenced by the following:

Attorney Docket No. 2003B005/2

- a. Pages 1-3 of **EXHIBIT A** describe the composition and method of making propylene copolymers containing dienes such as 2-methyl-1,5-hexadiene or α , internal nonconjugated dienes, e.g.; 7-methyl-1,6-octadiene.
- b. The examples on pages 2-3 of **EXHIBIT A** correspond to the examples provided on pages 95-99 of the above-identified application. Particularly, examples 1-3 and 6-7 in **EXHIBIT A** correspond to samples 5-9 in Example 2 of the above-identified application and examples 4-5 in **EXHIBIT A** correspond to samples 10-11 in Example 3 of the above-identified application.
5. It is my belief that the above-cited facts, as supported by **EXHIBIT A**, provide clear evidence of my conception and actual reduction to practice of the invention described and claimed in the above-identified application prior to May 3, 2002.
6. I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

6/26/2006

Date



Palanisamy Arjunan

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PATENT MEMORANDUM

COPY

EXXON CHEMICAL COMPANY

INVENTOR(S)
P. Arjunan

OCT 05 2006

DIVISION MEMO NO.

PM 99107

CLASS

PATENT COMMITTEE

Polymer Science

EXACT DESCRIPTIVE TITLE

New Diene-Modified PP Compositlons: C₇/(MOD/MHD) Copolymers

BRIEF ABSTRACT OF INVENTION

Synthesis of novel C₇/(MOD/MHD) Copolymers via metallocene catalysed batch slurry process was disclosed. Our experimental results indicated that copolymerization of C₇ with dienes, MOD or MHD via a batch, slurry process produced novel copolymers. The unique structure/properties and their use in various applications were also part of this invention

STATUS OF INVENTION (EXISTING OR CONTEMPLATED
EXPERIMENTAL, COMMERCIAL OR PLANT SCALE USE)

Experimental

DATE OF FIRST USE, PUBLICATION, AND/OR SALE

NA

WERE YOU WORKING FULL OR PART TIME ON ANY GOVERNMENT
CONTRACT AT, OR WITHIN ONE YEAR PRIOR TO THE TIME THE
INVENTION WAS FIRST CONCEIVED OR TESTED?☐ YES ☐ NO

CONTRACT NO.(S)

FOR LAW-TECHNOLOGY DEPARTMENT USE ONLY

DATE RECEIVED

7/13/99

ATTORNEY'S INIT.

FIRST WRITTEN DESCRIPTION

DATE 3/24/99

HEREWITH OR FILED AT

BPC 206

DATE OF FIRST TEST

3/24/99

WHERE RECORDED?

NBP#: 21587 - 18-22,
43-48, 60-61

FIRST SKETCH OR DRAWING

DATE 3/24/99

HEREWITH OR FILED AT

BPC 206

COMPANY REPORTS, FILE MEMOS, PMS RELATED TO
INVENTION (IDENTIFY)

P.Arjunan, Updates, March - June /99

FIRST DISCLOSURES TO OTHERS

DATE 5/28/99

TO WHOM AND WHERE

P.K. Agarwal/BPC 1126, W, Weng/BPC 2116, and
A.H. Dekmezian/ BPC 1107

IS MODEL OR PROTOTYPE AVAILABLE?

☐ YES☐ NO

DETAILED DESCRIPTION OF INVENTION (SEE INSTRUCTIONS ON REVERSE SIDE)

Background Information:

Syntheses of high melt strength (HMS) i-PP compositions, specifically the i-C₇/α,ε-Diene copolymer¹⁻³, amorphous C₇/α,ε-Diene copolymer, ⁴ and C₇/α, internal nonconjugated-diene copolymers⁵⁻⁷ were reported previously. Recently, synthesis of diene modified LCB-PP compositions using the PROP facility for targeted applications - thermoforming, foaming, molding and others has been demonstrated. One inherent limitation of the diene modified LCB-PPs is the gel formation in the reactor at high concentrations (> 200 - 300 PPM) of the α, ε -dienes. Also the above LCB-PP structures might degrade during the processing and fabrication stages of the targeted applications. There is a need to have either higher level of LCBs beyond the above gelation limit or some residual olefinic bonds that would crosslink to counter balance the chain scission of PP backbone during the melt processing. One approach to overcome the above problems is to use α, internal nonconjugated- diene such as 7-methyl-1, 6-octadiene (MOD) or 5-methyl-1,5-hexadiene (MHD).

Summary of the Invention:

The object of this invention is the metallocene catalysed synthesis of new PP copolymers containing dienes such as 7-Methyl-1, 6-octadiene (MOD) or 5-methyl-1, 5-hexadiene (MHD). Specifically, synthesis of the copolymer, C₇/(MOD or MHD), using Q catalysts - MAO or DICOP-activated, both supported and unsupported versions, via bulk/slurry processes is claimed. Another object of this invention is the unique structure/properties of the above copolymers, specifically their LCBs, multiple unsaturation sites in the side-chain, high melt-extensional viscosity/rigidity/flex modulus/T_g/HDT, radiation resistance, precursor for functional/graft PP copolymers, better compatibility with other unsaturated polyolefins in DVA/thermoset applications, and other enhanced attributes. Yet another object of this invention is the metallocene catalysed polymerisation processes to make the above terpolymers in a batch or continuous reactor, specifically Q-catalysed, solution/slurry/bulk processes.

(Continue Description on Additional Sheets)

INVENTOR(S)

SIGNATURE (FIRST NAME IN FULL)

P. Arjunan

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INVENTOR EMPLOYMENT CONTRACT

☐ YES ☐ NO

CITIZENSHIP:

☐ U.S.A.☐ OTHER India

INVENTOR EMPLOYMENT CONTRACT

☐ YES ☐ NO

CITIZENSHIP:

☐ U.S.A.☐ OTHER

EXXON CHEMICAL CO. DIVISION:

OTHER:

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OTHER:

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PATENT MEMORANDUM

Page No. 2

(For Continued Detailed Description
of Invention)INVENTOR(S)
P. ArjunanEXACT DESCRIPTIVE TITLE
New Diene-Modified PP Compositions: C₃ (MOD/MHD)
Copolymers

The new copolymer compositions from the above polymerizations, the improved properties/performance of these products, their use in targeted applications, their blends with other polymers/materials, any fabricated articles such as film, fibers, sheets, plaques, tapes, wovens that contain the above compositions, are within the scope of this invention. Any variations of the above disclosures that are obvious, and can be derived by those skilled in the art are also part of this invention.

Experimental:1. Materials/Methods:

The dienes, MOD and MHD, were purchased (Aldrich Co.), and were purified by passing through an activated alumina column. The catalyst, Q, dimethylsilylbis(2-methyl 4-phenyl indenyl) zirconium dichloride was purchased (Boulder Scientific Company) and was used as such. The supported-Q catalyst was prepared by using a literature procedure. The examples, 1 - 3 and 6 - 7, were synthesised via a batch, slurry process at 75° C using the unsupported Q-catalyst while 4 - 5 were prepared using the supported-Q catalyst. Various molecular and thermal properties of the above polymers were determined following standard polymer characterisation methods. The molecular weights were determined on the virgin samples by using the GPC-3D method.

2. Synthesis:a. Supported-Catalyst Preparation:

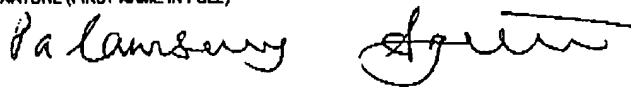
In a nitrogen purged dry glove box, the metallocene catalyst was placed in a 100-ml beaker to which the 30 wt% MAO solution was added. The mixture was stirred magnetically for 1 hr and was diluted with 10 g toluene. The "Davison MS952 silica, pre-calcined at 600° C", 5.0 g, was placed in a 250 ml beaker separately; 1/4th portion of the above (metallocene+ MAO)/toluene mixture was added carefully and the mixture was stirred manually to homogeneity and uniform color. The rest of the (metallocene+MAO) mixture was also added to the silica as above to achieve a mobile slurry. The entire mixture was transferred to a 250 ml round-bottom flask, and was dried under vacuum. The yield was calculated and the metal loading was analysed.

b. Batch Polymerisation - Hexane Slurry Process:

In a typical experiment, the examples, 1 - 7, of this invention were synthesised by batch slurry-polymerisation of C₃ using the Q-catalyst. These polymerizations were typically conducted in a 2 L Zipperclave reactor using a mixture of propylene (400 ml) in hexane (800 ml), and weighed amount of the dienes (1 - 5 ml). The reactor was heated to the set temperature, 75° C, and equilibrated for 5 min. The scavenger, triethyl aluminum (1 ml, 1 M solution in toluene) was charged to the reactor through a stainless tube. A fresh stock solution of the Q-catalyst (2 mg) in toluene (5 ml) was prepared separately and a portion (1 ml) of it was injected using a catalyst tube. The polymerization was carried out for 60 min after which the reactor was cooled to 25° C and vented. The polymer was collected, was dried by N₂ purge for overnight, and was weighed. Several batch polymerisations were conducted as above using both the supported and unsupported Q-catalysts, and the experimental details were recorded in the NBP#: 21587 - 20-21, - 30, - 43-44, and - 60-61. The polymer samples from the above runs were characterised by using the ¹H NMR, DSC, MFR, and GPC methods. The results are included in Table 1.

INVENTOR(S)

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EXXON CHEMICAL CO. DIVISION:

EXXON CHEMICAL CO. DIVISION:

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PATENT MEMORANDUM

Page No. 3(For Continued Detailed Description
of Invention)INVENTOR(S)
P. ArjunanEXACT DESCRIPTIVE TITLE
New Diene-Modified PP Compositions: C₃*/(MOD/MHD)
CopolymersTable 1: C₃*/(MOD + DD) Polymerisation Data

Examples	Comonomer: MOD/DD, PPM	MFR dg/min	¹ H NMR Data: % Trisubstituted	Chain End % Vinyl	Unsaturation: % Vinylidene	GPC-DRI Mw/Mn/PD	GPC-VIS Mw/Mn/PD	T _m /T _c , °C
<u>1</u>	0/0	21.9	11	33	56	266/111/2.4	321/126/2.5	155/106
<u>2</u>	18/0	5.3	51	23	26	440/197/2.2	520/210/2.5	152/107
<u>3</u>	128/0	1.7	79	7	14	506/264/1.9	650/306/2.1	150/109
<u>4</u>	7/0	ND	39	16	45	512/141/3.6	561/137/4.1	149/109
<u>5</u>	108/0	ND	69	10	21	476/131/3.6	533/132/4.0	144/106
<u>6</u>	0/18	1.4	30	12	48	448/121/3.7	528/126/4.2	143/107
<u>7</u>	0/108	1.0	50	1	49	480/130/3.7	579/134/4.3	142/106

ND: Not determined

The above results indicated:

- These copolymers had multiple unsaturation sites, mostly trisubstituted, vinylidene, and vinyl.
- The copolymers, examples, 4 - 7, contained long chain branching as evidenced by the GPC-VIS data. Their branching index, g-factor was < 1
- The copolymers, examples 6 - 7, had complex structures as evidenced by the ¹H NMR data. The presence of significant amount of "trisubstituted unsaturation sites" was not expected as the comonomer, MHD did not have such sites to begin with. This unexpected result was due to the isomerisation of the "vinylidene unsaturation site" to a more stable "trisubstituted unsaturation site".
- It was possible that such isomerization process resulted in some long chain branches, which was evidenced by the GPC-3D data, as shown in *Figures 1-2*. The low MFR of these copolymers was due to their H-type branching.
- The supported Q-catalyst seemed to produce different PP compositions, examples 4 - 5, Vs that of the unsupported Q-catalyst, examples, 2 - 3, with the same comonomer, MOD. The CDBI of the former products (83, 89) was significantly higher than that of the later (50, 77).
- The results of thermogravimetric analysis (TGA) indicated improved thermal stability of the copolymers, examples 2 - 3, Vs the control, example 1.

The above examples are for illustrative purpose only. Synthesis of other similar PP copolymer structures via the batch bulk-slurry process involving the metallocene catalysts are within the scope of this invention. Any other variations of the above processes and PP copolymer compositions that can be derived from this teaching, and obvious to those skilled in the art are within the scope of this invention. These new LCB-PP polymers can be used in various applications such as thermoforming, foaming, radiation resistance, molding, extrusion coating, and others. Various fabricated articles such as films, fibers, sheets, plaques, tapes, wovens, and any dimensional objects, which contained or consisted of the above PP copolymer compositions are also part of this invention.

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PATENT MEMORANDUM

Page No. 4

(For Continued Detailed Description
of Invention)INVENTOR(S)
P. Arjunan

EXACT DESCRIPTIVE TITLE

New Diene-Modified PP Compositions: C₇*/(MOD/MHD)
CopolymersReferences:

1. P.Meka et al., US Patent: 5,670,595 (1997)
2. T. Ushioda et al., PCT: WO99/11680 (1999)
3. B.P. Etherton et al., US Patent: 5,504,171 (1996)
4. R. Koopmans et al., PCT: WO98/49229 (1998)
5. M. Hackmann et al., Macromol. Chem. Phys., 199(8), 1511-17 (1998)
6. J. Park et al., Eur. Polym. J., 33(4), 447-451 (1997)
7. J.P. Dassaud et al., Polym. Adv. Technol., 4 (7), 457-64 (1993)

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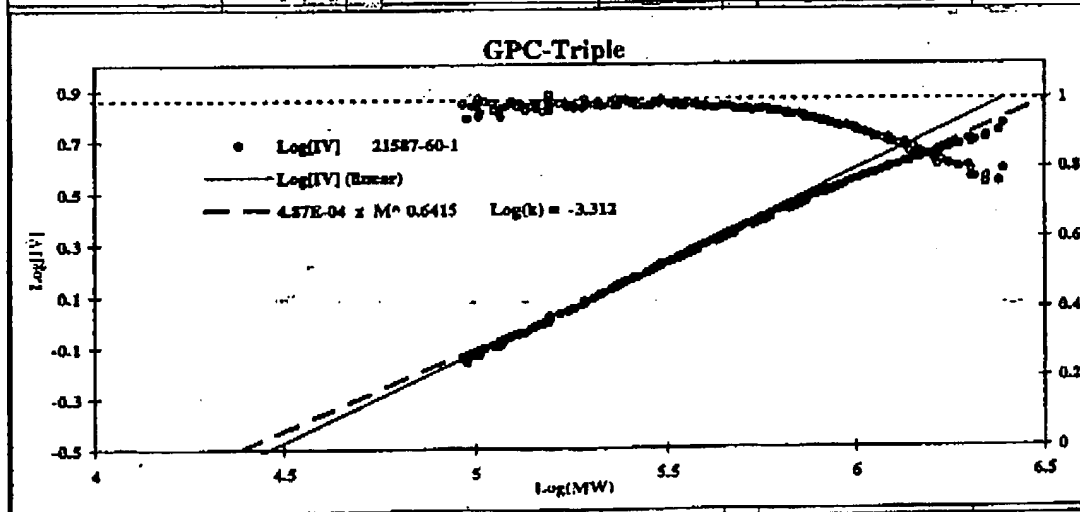
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21587-60-1					
Filename: XL91		Run Time: Tue Jun 08 1999 21:44:31			
DRI Parameters		LS Parameters		Viscometer	
Conc. (mg/ml) =	1.1457	(dn/dc) =	0.104	IP Sensitivity =	10.000
Inject. Vol. (ml) =	317	K* =	7.3708E-08		
Inject Mass (mg) =	0.363	A2 =	4.00E-04		
DRI Constant =	4.806E-07	LS Constant =	8.739E-08	DP Sensitivity =	0.8931
Calc. Mass (mg) =	0.366	LS Delay (ml) =	-0.2900	DP Delay (ml) =	-0.075
DRI Mn =	128257	LS Mn =	137270	GPC-Vis Mn =	87470
DRI Mw =	463964	LS Mw =	476454	GPC-Vis Mw =	498255
DRI Mz =	905766	LS Mz =	950512	GPC-Vis Mz =	1076803
Mw/Mn =	3.62	Vis Ave. MW (LS) =	419677	Vis Ave. MW (Vis) =	433903
DRI [η] =	2.056	GPC-LALLS [η] =	2.008	Viscometer [η] =	1.949
Invert? (1/0=Y/N)	0	Batch LS Mw =	138233	G' (Vis. Ave.) =	0.931
Mark Houwink				Column Calh.	
PS Log(k) =	-3.757			A0 =	11.407
PS a =	0.6700			A1 =	-0.256
Sample Log(k) =	-3.648			A2 =	-0.0021144
Sample a =	0.7058			A3 =	0
		Baseline	Settings		
X_left =	16.00	X_left =	15.65	X_left =	15.60
Y_left =	0.00	Y_left =	0.05	Y_left =	-0.15
X_right =	26.00	X_right =	24.00	X_right =	25.00
Y_right =	0.00	Y_right =	0.05	Y_right =	-0.80
		Left LS Limit =	18.75	Left DP Limit =	16.3
Integration	Limits	Baseline	Offset	LCB	Limits
left limit =	16.22	DRI Offset =	100.574	left limit =	16.75
right limit =	25.00	LS Offset =	16.159	right limit =	21.00
		DP Offset =	-1.7		



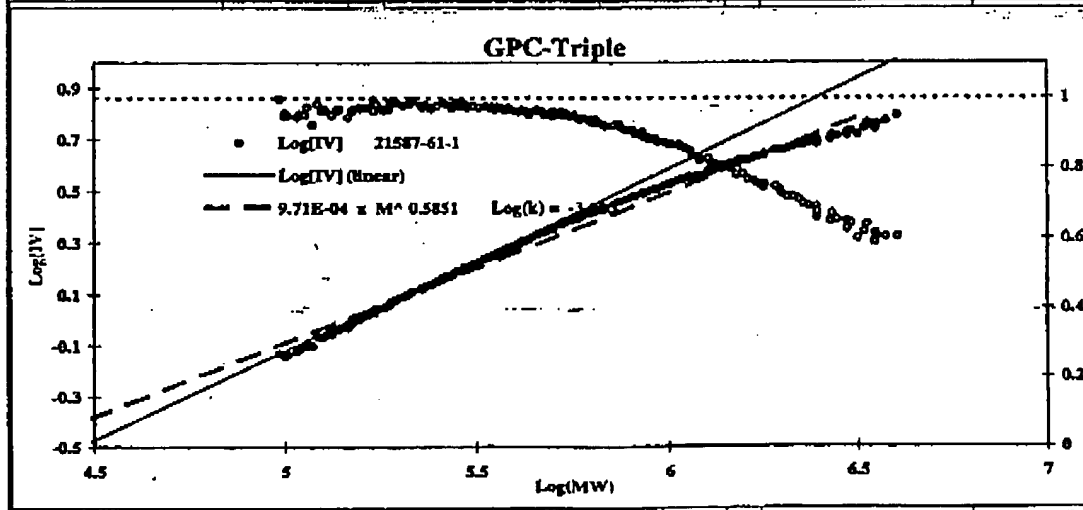
Inventories:

Witnessed:

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21587-61-1					
Filename: XL92		Run Time: Tue Jun 08 1999 23:45:24			
DRI Parameters		LS Parameters		Viscometer	
Conc. (mg/ml) =	1.0729	(dn/dc) =	0.104		
Inject. Vol. (ml) =	317	K* =	7.3708E-08	IP Sensitivity =	10.000
Inject Mass (mg) =	0.340	A2 =	4.00E-04		
				DP Sensitivity =	0.8931
DRI Constant =	4.806E-07	LS Constant =	8.739E-08	DP Delay (ml) =	-0.075
Calc. Mass (mg) =	0.343	LS Delay (ml) =	-0.2900		
				GPC-Vis Mn =	105171
DRI Mn =	142093	LS Mn =	141004	GPC-Vis Mw =	543400
DRI Mw =	497594	LS Mw =	567951	GPC-Vis Mz =	1298205
DRI Mz =	1052942	LS Mz =	1411400		
Mw/Mn =	3.50	Vis Ave. MW (LS) =	484672	Vis Ave. MW (Vis) =	467924
DRI [η] =	2.141	GPC-ALLS [η] =	1.936	Viscometer [η] =	2.000
				G* (Vis. Ave.) =	0.863
Invert? (I/O=Y/N)	0	Batch LS Mw =	568512		
				Column Calib.	
Mark Houwink				A0 =	11.407
PS Log(k) =	-3.757			A1 =	0.256
PS a =	0.6700			A2 =	-0.0021144
Sample Log(k) =	-3.648			A3 =	0
Sample a =	0.7058				
		Baseline	Settings		
X_left =	15.75	X_left =	15.65	X_left =	15.60
Y_left =	-0.20	Y_left =	0.00	Y_left =	0.32
X_right =	26.00	X_right =	24.00	X_right =	25.00
Y_right =	0.10	Y_right =	0.15	Y_right =	-0.10
		Left LS Limit =	15.65	Left DP Limit =	15.8
Integration	Limits	Baseline	Offset	LCB	Limits
left limit =	16.00	DRI Offset =	100.414	left limit =	16.50
right limit =	24.50	LS Offset =	16.079	right limit =	21.00
		DP Offset =	-3.76		



Inventor

Witnessed

Patricia Schmitt

E M Canal 7/3/99

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